SCIENCE FOR CERAMIC PRODUCTION

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CONTROL OF STRUCTURAL AND FLOW PROPERTIES OF CERAMIC MIXTURES USING AQUEOUS EMULSION OF CUTTING LIQUID WASTE

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The possibility of using an aqueous emulsion of cutting liquid waste in the production of construction ceramics is determined. The effect of CL waste on the structural and flow (molding) properties and the energy consumed in the molding of clay and ceramic mixtures based on Kiev spondyl clay is studied.

Aqueous emulsion effluents of cutting liquids (CL) belong to the category of petrochemical industrial wastes whose utilization is expedient both for environmental reasons and for the improvement of the technological properties of molding mixtures [1]. Plastification of a ceramic mixture through the development of a chemically active medium under the effect of its treatment with cutting liquid decreases the molding energy and contributes to the development of resource-saving technologies.

The CL wastes contain synthetic and semi-synthetic components: higher fatty alcohols, monoalkyl sulfates, certain ingredients of synthetic detergents, sodium salt of inorganic acids, as well as emulsified mineral oils contributing to enhanced wear resistance of cutting tools.

To determine the feasibility of using CL aqueous emulsion waste in the production of wall ceramics, the effect of CL waste on the structural and flow (molding) properties and the energy consumed in molding was studied on clay and ceramic mixtures based on Kiev spondyl clay with the optimum moisture content (25.5 and 22%, respectively). The following relationship was used for this purpose [2]:

$$P_m = f(W),$$

where P_m is the plastic strength, Pa; W is the absolute moisture, %.

Considering the possibilities of using the regional cutting liquid waste, their two varieties (Akvol-10M and ET-2 reactants) were used.

The structural and flow properties of argillaceous systems modified by CL waste additives were investigated employing an improved Tolstoy's instrument and an AP-2 penetrometer. The effect of CL aqueous-emulsion waste on the energy consumed in molding a ceramic mixture was studied by comparing the energy consumption of the deformation process using the obtained values of the energy expenditure equivalent [2].

The chemical, batch, and granulometric composition of the material is shown in Tables 1 and 2.

The presence of surfactants in the composition of CL aqueous emulsion decreases free energy at the phase boundary, which is testified by the data in Table 1. The functional dependence

$$\sigma = f(C),$$

where σ is the surface tension, H/m, and C is the vol.% content of the introduced waste additives, makes it possible to determine the critical micelle concentration (CMC) related to the association of reactant molecules in the liquid dispersion medium. The CMC is equal to 50 and 75% for Akvol-10M and ET-2 reactants, respectively.

The specifics of the rheological behavior of ceramic mixtures in the presence of CL aqueous emulsion waste are determined by the aggregate processes taking place in the clay – water – chemical agent system, primarily by the interphase interactions with participation of the dissolved agent molecules. One should take into account the weight content and the chemical composition of the introduced CL additives, as well as the composition of the mixture treated with the additives.

According to the obtained experimental data, introduction of CL waste additives, whose concentration is in the ante-micellar region (10 – 25%), through the adsorption effect, decreases the strength of the emerging spatial coagulation structures, which is caused by the blocking of coagula-

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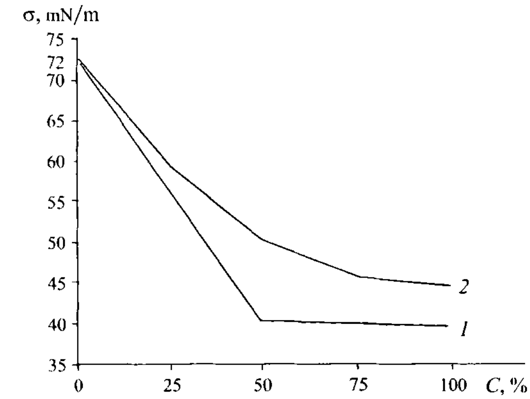

Fig. 1. Variation in the surface tension of aqueous solution of CL waste depending on the content of Akvol-10M (*1*) and ET-2 (*2*) ad-

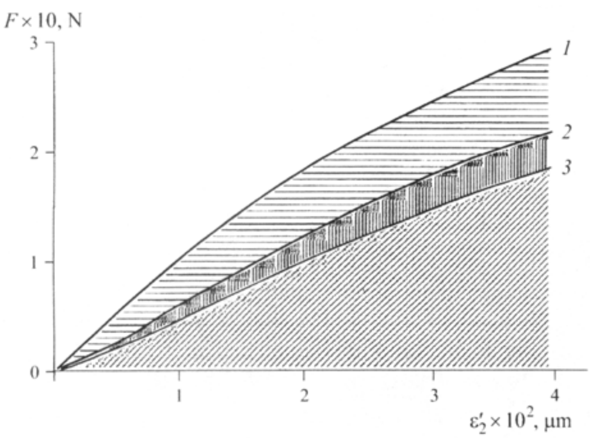

Fig. 2. The effect of the optimum reactant additives on the variation of the energy expenditure equivalent in molding of ceramic mixtures: *1*) without reactant; *2* and *3*) with the optimum additives of Akvol-10M (50%) and ET-2 (75%), respectively.

tion centers by adsorbing molecules of chemical reactants. This is corroborated by the decrease in the structural-mechanical constants, i.e., the flow parameters which characterize strength and viscosity properties of the emerging coagulated structure, namely, the modulus of fast E_1 and slow E_2 elastic deformation, the equilibrium modulus of elastic deformation E_e, the arbitrarily static yield point P_{k_1}, the maximum plastic viscosity η_1, the plastic strength P_m, and the true relaxation period θ_1 (Table 3). At the same time, an increase in plasticity P_{k_1}/η_1 is observed as the result of the plastifying effect of CL aqueous emulsion on the emerging structure [3], which is indicative of improved molding properties of ceramic mixtures under the effect of their treatment by the waste in the specified concentrations.

Within the CMC region (50 – 100%), the formation of adsorbing hydrate shells facilitates the emergence of a structural mechanical barrier on the surface of the disperse phase particles, which weakens the Van der Waals interparticle attraction forces. In the case of the CMC, the structural and flow parameters take the smallest values, which indicates that a system weakens under the effect of CL additives. The criterial values of elasticity λ, plasticity, and true relaxation period in this case correspond to the criterial quality parameters of highly moldable mixtures [3].

The deformation process in the clay – water – CL waste system is determined by the ratios between the fast ε'_0, slow ε'_1, elastic and plastic $\varepsilon'_{i\tau}$ deformations arising in a ceramic mixture in the presence of 50 – 100% additives of CL aqueous emulsion waste. An improvement of the molding properties and plastification of the mixture is indicated by an increased share of slow and plastic deformations in the overall deformation balance. This evolution of the deformation process typical of chemically treated ceramic mixtures determines the specifics of their behavior in drying, ensures better drying properties of the intermediate ceramic product, and a sharp decrease in the amount of pieces rejected after drying [4].

According to analysis of structural and flow properties, the optimum amount of the considered CL additives is 50 – 75%, which corresponds to the CMC.

Association of reactant molecules in the liquid disperse medium and on the surface of the disperse phase surface,

TABLE 1

Material	Weight content, %									
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	SO_3	CaO	K_2O	Na_2O	calcination loss
Marl clay (spondyl)	46.57	9.65	3.58	0.54	1.81	0.80	16.46	1.75	0.35	18.49
Loess-like loam	79.23	6.47	2.14	0.50	1.21	0.36	3.39	1.54	0.68	4.48
Ash from Darnitskii Power Plant-4	43.38	14.53	7.39	0.54	1.13	0.34	2.39	2.21	0.64	27.45

TABLE 2

Material	Granulometric content, %, for grain diameter, mm					Impurity, 5, on a sieve with mesh size 0.5 mm	
	> 0.5	0.5 – 0.01	0.01 – 0.005	0.005 – 0.001	< 0.001	total	including carbonates
Spondyl marl clay (93%)	16.91	53.73	19.50	8.60	1.25	0.01	0
Loess-like loam (7%)	11.74	69.41	1.30	3.56	13.85	0.10	0.04
Ash from Darnitskii Power Plant-4 (7%, above 100%)	53.26	30.94	7.45	6.85	1.50	–	–

TABLE 3

Content, %	P_m, μPa	Structural-mechanical constants					Structural-mechanical parameters			Deformation parameters		
		$E_1 \times 10^{-1}$, μPa	$E_2 \times 10^{-1}$, μPa	$E_e \times 10^{-1}$, μPa	$P_{k_1} \times 10^{-2}$, mPa	η_1, nPa · sec	λ	$(P_{k_1}/\eta_1) \times 10^4$, $\sec^{-1}$	θ_1, sec	ε_0', %	ε_2', %	ε_{it}', %
					Mixture based on spondyl clay							
Without additive	5.6	52.6	98.0	34.2	5.5	450.0	0.35	1.2	1306	39.4	20.6	40.0
Akvol-10M:												
0.10	4.2	55.6	118.0	37.8	4.5	386.0	0.36	1.1	1021	34.4	17.6	48.0
0.25	3.9	33.2	52.0	19.9	4.0	175.0	0.40	2.3	875	29.6	20.1	50.3
0.50	3.6	41.7	83.3	27.8	3.2	133.0	0.34	2.4	478	23.7	11.8	64.5
0.75	4.1	77.0	130.0	48.4	9.0	220.0	0.37	4.1	413	25.3	12.7	62.0
1.00	4.2	70.0	125.0	44.9	8.5	300.0	0.36	2.8	668.5	28.4	15.7	55.9
ET-2:												
0.10	5.6	31.3	90.9	23.3	2.5	416.0	0.26	0.6	1786	58.7	20.2	21.1
0.25	4.8	50.0	71.4	29.4	3.0	303.0	0.41	0.9	1030	32.5	19.5	48.0
0.50	4.4	45.5	62.5	26.3	5.5	136.0	0.42	4.0	5171	21.4	15.5	63.1
0.75	5.8	66.7	90.9	38.5	4.5	306.0	0.42	1.5	794.8	27.3	20.0	52.7
1.00	5.9	31.3	71.4	21.7	10.0	307.7	0.30	3.2	1417	42.7	18.7	38.6
					Batch based on spondyl clay							
Without additive	3.5	20.0	60.0	15.0	1.0	250.0	0.25	0.4	1665	42.2	11.8	46.0
Akvol-10M:												
0.10	3.4	32.4	61.0	21.1	2.9	210.0	0.34	1.3	1047	21.5	9.5	69.1
0.25	3.1	31.3	43.5	18.2	4.5	60.0	0.42	7.5	333	16.0	11.5	72.5
0.50	2.9	26.7	56.0	18.0	5.0	40.0	0.33	2.5	221	13.8	6.6	79.6
0.75	3.0	28.0	58.8	19.0	4.0	86.0	0.32	4.7	452	24.0	11.0	65.0
1.00	3.2	38.5	66.7	24.3	3.0	170.0	0.33	1.8	696	27.8	15.6	56.6
ET-2:												
0.10	3.2	14.4	42.2	10.7	1.0	160.0	0.25	0.6	1495	38.8	11.4	49.8
0.25	2.7	15.3	30.3	10.1	1.2	120.0	0.33	1.0	1188	31.3	12.8	55.9
0.50	2.3	12.7	27.8	8.7	0.3	43.3	0.32	0.8	497	17.2	11.0	71.8
0.75	2.6	16.6	40.2	11.7	0.3	124.0	0.24	1.8	1059	48.8	15.2	36.0
1.00	2.5	18.8	45.0	13.3	0.9	160.0	0.56	0.9	1203	34.0	14.4	85.6

when the content of the introduced chemical reactant is 75 – 100%, increases the strength and viscosity parameters, due to the emergence of additional reactions between the structured adsorbing hydrate shells and the micellar formations emerging from the molecules of the reactant in the liquid phase. This is corroborated by a relative increase in the modulus of fast and slow elastic deformation, arbitrary static yield point, the maximum plastic viscosity, the true relaxation period, and plastic strength.

Owing to the association effect, as a mixture is treated by CL in the amount of 50 – 100%, the predominant development of plastic deformations related to the exit of particles from the area of action of interparticle attraction forces, loses its destructive effect and improves the conditions for mutual sliding of particles, which facilitates the plastification of the ceramic mixture.

The obtained data correlate with the results of determining the energy consumed on deformation in the presence of Alvol-10M and ET-2 reactants (Fig. 2). The increase in the plastifying effect of the reactants whose content is 50 – 70%, due to the formation of structurized adsorbing hydrate films is accompanied by an increasing quantity of bonded moisture, which ensures hydrodynamic sliding of particles with respect to each other. This contributes to a decrease in the equivalent energy consumption in the course of molding employing chemical treatment with CL waste:

$$A = F\varepsilon_2' ,$$

where A is the energy expenditure equivalent; F is the shear load, N; ε_2' are slow elastic deformations such as shape-modifying deformations.

According to the obtained experimental data, introduction of 50 – 75% Akvol-10M and ET-2 to a ceramic mixture results in a decrease in the energy consumed in the molding process by 20 – 25%, as compared to the molding of a mixture without additives.

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